

THE EFFECT OF IONIZATION ON THE INFRARED ABSORPTION SPECTRA OF PAHs:
A PRELIMINARY REPORT

D. J. DeFrees* and M. D. Miller**

*Molecular Research Institute, Palo Alto, CA 94304

**IBM Almaden Research Center, San Jose, CA 95120

The emission lines observed in many interstellar infrared sources at 3050, 1610, 1300, 1150, and 885 cm^{-1} (3.28, 6.2, 7.7, 8.7, and 11.3 microns) are hypothesized to originate from polycyclic aromatic hydrocarbon molecules (PAHs). (Leger & Puget, 1984, Allamandola et al., 1985) These assignments are based on analyses of laboratory infrared spectra of neutral PAHs. However, it is likely that in the interstellar medium the PAHs are ionized, i.e., are positively charged. Furthermore, as pointed out by Allamandola et al. (1987), "although the IR emission band spectrum resembles what one might expect from a mixture of PAHs, it does not match in details such as frequency, band profile, or relative intensities predicted from the absorption spectra of any known PAH molecule." The PAH hypothesis is far from proven.

One source of additional information to test the PAH hypothesis is *ab initio* molecular orbital theory. (Hehre et al., 1986) It can be used to compute, from first principles, the geometries, vibrational frequencies, and vibrational intensities for model PAH compounds which are difficult to study in the laboratory. We have used the Gaussian 86 computer program (Frisch et al., 1984) to determine the effect of ionization on the infrared absorption spectra of several small PAHs: naphthalene and anthracene. This brief article contains a preliminary report of the results of these calculations.

The vibrational spectra were computed at the HF/3-21G level of theory. Previous studies (DeFrees & McLean, 1985, Yamaguchi et al., 1986) show that after simple scaling, *ab initio* frequencies are accurate to $\pm 50 \text{ cm}^{-1}$ and intensities are correct to within a factor of two. Calculations performed on benzene demonstrate that these conclusions, reached on studies of small molecules, apply as well to the study of PAHs. Computed transmittance spectra were generated with lorentzian curves (constant half-height width of 15 cm^{-1}) centered at the HF/3-21G wavelengths with an area equal to the computed intensity. The spectra are scaled to give a maximum transmittance of 5%. Figures 1 and 2 are computed transmittance spectra of naphthalene (C_8H_{10}) and its radical cation ($\text{C}_8\text{H}_{10}^+$), respectively, while figures 3 and 4 show computed vibrational spectra of anthracene ($\text{C}_{10}\text{H}_{14}$) and its radical cation ($\text{C}_{10}\text{H}_{14}^+$), respectively. Frequencies have not been scaled in these plots; for comparison with experiment multiply each frequency by 0.89. (DeFrees & McLean, 1985)

Ionization of naphthalene and anthracene has a striking effect on the predicted infrared absorption spectrum. In each case, strong C-H stretching bands around 3300 cm^{-1} in the neutrals are absent in spectra of the cations. In the region from 400 to 2000 cm^{-1} there are also some large changes. In naphthalene, the neutral has two strong absorptions in this region whereas the ion has 5; anthracene has three strong, narrow peaks while its cation has one strong, wide, peak resulting from the blending of several strong absorptions.

Analysis of these results is on-going. We will determine the cause for the large changes that occur in the absorption spectra on ionization. With this understanding, we hope to be able to make at least qualitative extrapolations to larger systems. We also intend to examine the effects of ionization on the emission spectra.

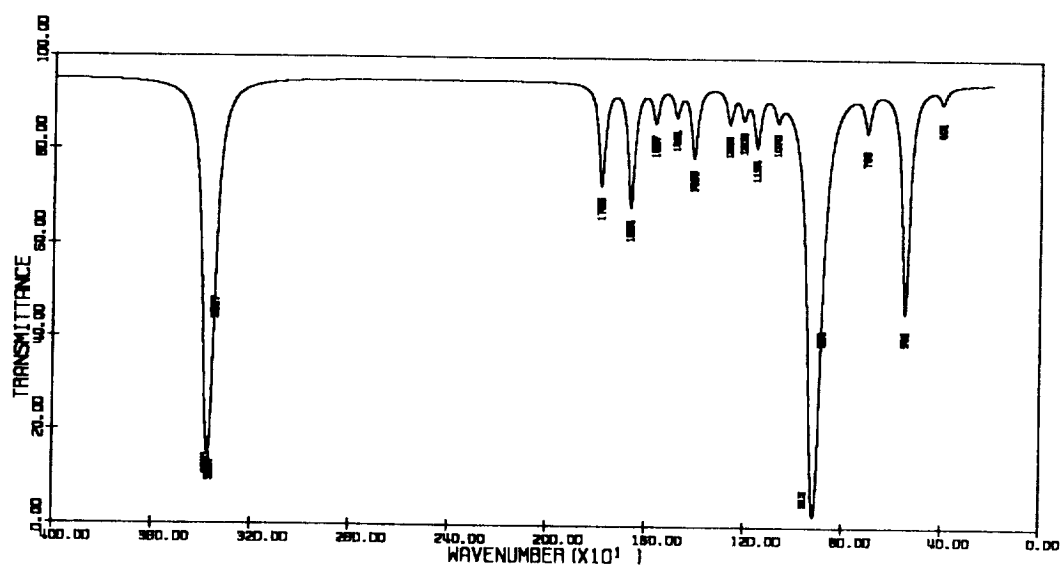


Fig. 1 Computed transmittance spectrum of naphthalene

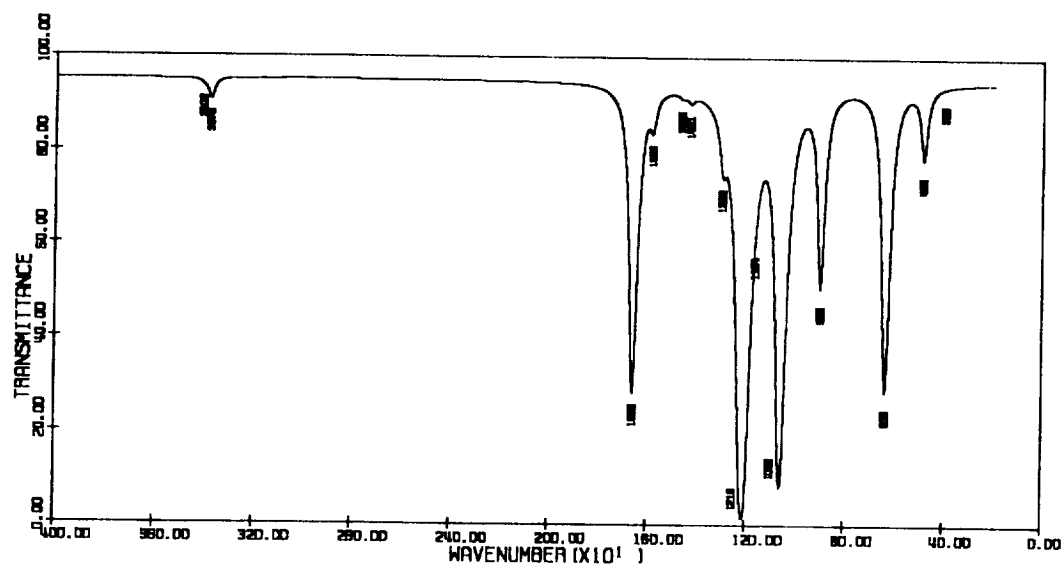


Fig. 2 Computed transmittance spectrum of naphthalene radical cation

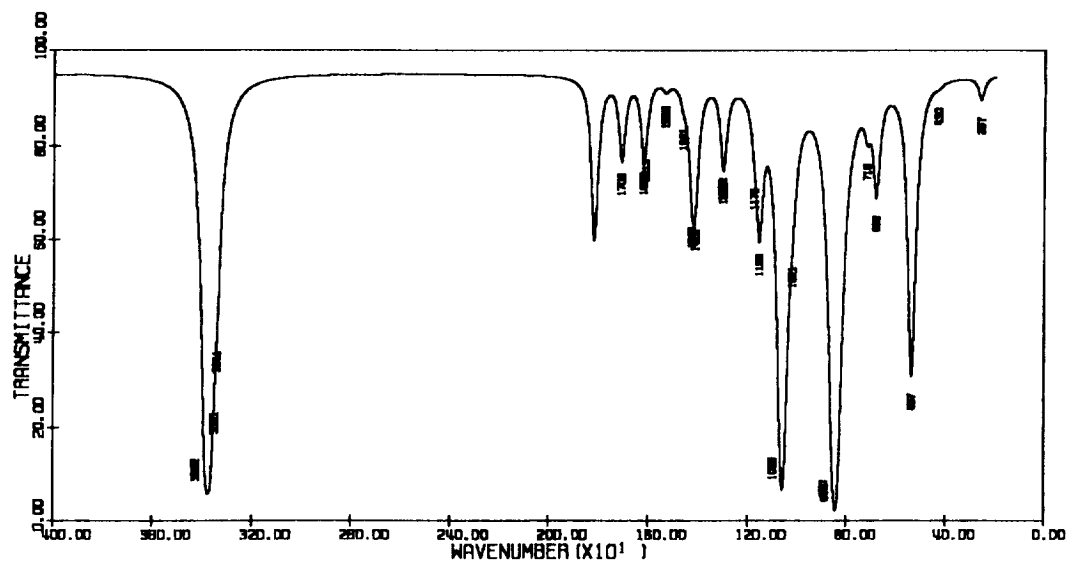


Fig 3 Computed transmittance spectrum of anthracene

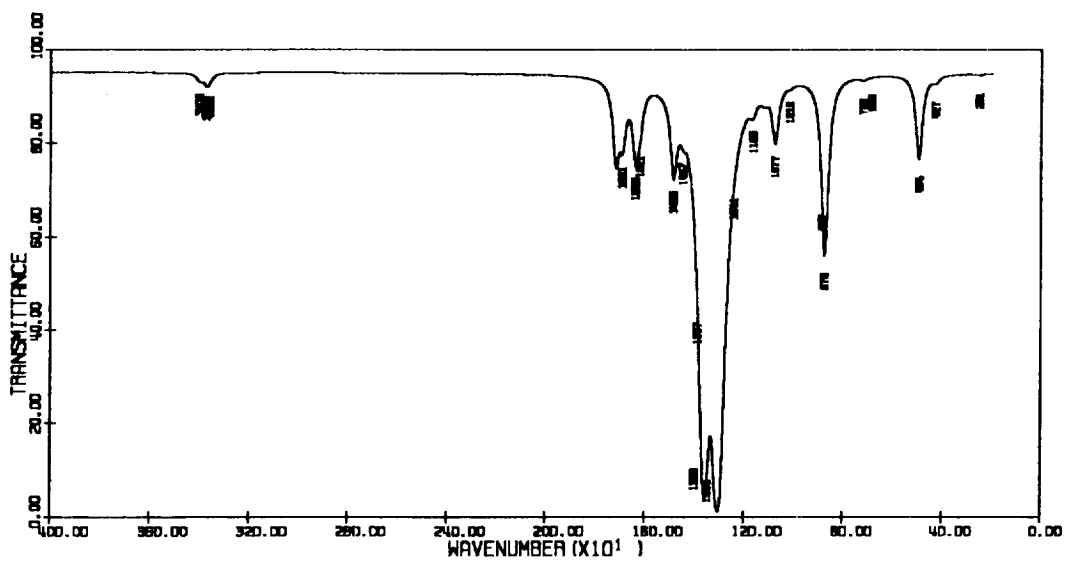


Fig 4 Computed transmittance spectrum of anthracene radical cation

References

- L. J. Allamandola, A. G. G. M. Tielens, & J. R. Barker. (1985) *Ap. J. Letters*, **290**, L25.
- L. J. Allamandola, A. G. G. M. Tielens, & J. R. Barker. (1987) Infrared emission from interstellar PAHs. in G. E. Morfill & M. Scholer, editor, *Physical Processes in Interstellar Clouds*, pages 305.
- D. J. DeFrees & A. D. McLean. (1985) *J. Chem. Phys.*, **82**, 333.
- M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, C. M. Rohlfing, L. R. Kahn, D. J. DeFrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fluder, & J. A. Pople. (1984) *Gaussian 86*. Pittsburgh, PA: Carnegie-Mellon Quantum Chemistry Publishing Unit.
- W. J. Hehre, L. Radom, P. v. R. Schleyer, & J. A. Pople. (1986) *Ab Initio Molecular Orbital Theory*. New York, NY: John Wiley and Sons.
- A. Leger & J. L. Puget. (1984) *Astro. Ap.*, **137**, L5.
- Y. Yamaguchi, M. Frisch, J. Gaw, H. F. Schaefer III, & J. S. Binkley. (1986) *J. Chem. Phys.*, **84**, 2262.